An unweighted mean of the measurements gives a value of 44.60 with a probable error not greater than 0.04 Å. This value differs from that of Thibaud by an amount which is approximately equal to his maximum possible error. It is much lower than that of Weatherby.

In conclusion I wish to thank my friends in Ryerson for the interest taken in this work, and especially Prof. A. H. Compton under whose direction the work has been carried on. I am also deeply indebted to Dr. T. H. Osgood who began this work and who initiated me into it.

Note Added in Proof. By comparison with the $K\alpha$ line of aluminum, Söderman[5] has obtained a value of 44.70 ± 0.09 for the $K\alpha$ line of carbon.

[1] Weatherby, *Phys. Rev.*, **32**, 707 (1928).
[2] Thibaud, *J. Op. Soc.*, **17**, 145 (1928).
[3] Dauvillier, *J. Physique*, **8**, 1 (1927).
[4] Osgood, *Phys. Rev.*, **30**, 567 (1927).
[5] Söderman, *Zeit. f. Phys.*, **52**, 795 (1929).

ON THE IMPERFECTIONS OF CRYSTALS

BY F. ZWICKY

NORMAN BRIDGE LABORATORY OF PHYSICS, CALIFORNIA INSTITUTE OF TECHNOLOGY

Communicated February 13, 1929

(*a*) *Introductory Remarks.*—Imperfections of crystals may be either of mechanical or chemical nature. As will appear in the course of this investigation, the phenomena related to the chemical imperfections can hardly be understood without a preliminary knowledge of the mechanical defects of the crystals considered. The aim of the following considerations is to give theoretical reasons for the necessity of microscopic cracks even in the most perfect crystals. It will also be shown how the characteristics of these cracks, such as their size, shape, etc., may in principle be determined from the properties which characterize the atoms or ions which constitute the lattice. The author was led to his conclusions presented here in the course of an attempt to reconcile the discrepancy between the theoretical breaking strength of crystals with the observed values for this quantity. It is proposed therefore to consider this special problem first.

(*b*) *The Breaking Strength of Crystals.*—As Polanyi[1] has shown an estimate of the breaking strength Z can be obtained in this simple way. Let σ be the surface tension or the free energy per unit surface. Then the work done in forming two surfaces of 1 cm.^{2} each by breaking a crystal is equal to 2σ. The forces acting between the two surfaces during the process of rupture become negligible after a separation δ corresponding to

a few atomic instances. We have therefore this approximate equation: $2\sigma = Z.\delta$. Now it has been calculated from the theory of heteropolar crystals[2] that for lattices of the NaCl type we have: $\sigma = 0.12e^2/R^3$, $e = 4.77$ es. u. For NaCl itself the lattice constant is $R = 5.6 \times 10^{-8}$ cm. Therefore* $\sigma = 156$ erg/cm.^{2} and $Z \sim 2 \times 156 \times 10^8$ dynes/cm.^{2} $\sim$ 30,000 kg./cm.^{2} The experimental value is $Z = 50$ kg./cm.^{2} This enormous discrepancy made a rigorous treatment of the problem involved a necessity. The author[3] therefore gave an exact deduction of the breaking strength of rocksalt, making use of the theory of heteropolar crystals as developed by Madelung, Kossel, Born and others. The value obtained for Z at $T = 0$ is $Z = 20{,}000$ kg./cm.^{2}, in qualitative agreement with the above estimate. Now the theory of the ionic lattices mentioned before is of a very general nature. All the conclusions drawn from it concerning the elastic constants, the frequency of the residual rays, the heat of sublimation, etc., have been checked quantitatively by the experiment. The total failure to account for the breaking strength therefore confronted the theory with a serious difficulty. An attempt to account for the low "technical" strength by the influence of temperature did not lead to the desired result.

There then followed several very thorough experimental investigations of the strength of NaCl crystals. It was proved by different authors[4] that under certain special conditions the breaking strength could indeed be increased enormously. An NaCl crystal, for instance, whose surface is wetted will stand stresses as high as 16,000 kg./cm.^{2} before breaking, a value very near to the theoretically deduced strength. On application of great thermal gradients to a NaCl sphere stresses were produced in the center of the sphere as high as 7000 kg./cm.^{2} without causing rupture.† The experimental results then seemed to prove that, proper conditions being observed, an NaCl crystal will in fact exhibit the strength required by the theory. There arose now the question as to the cause of the low breaking strength of the crystals in the dry state.

Griffith[5] suggested that the existence of fine cracks on the surface of crystals might provide a satisfactory explanation. Application of a relatively low average stress would then indeed produce much higher stresses at the edges of the cracks and there cause the rupture. Smekal[6] elaborated this theory. He thinks that actual crystals are never of an ideal geometrical structure but are made up of a great many microscopic blocks leaving cracks and other imperfections between them. We might call such a structure a mosaic crystal according to a term used by Ewald.[7] Smekal correlated this conception with a great many facts such as electric conductivity, electric strength, photoelectric absorption, etc. He succeeded in determining the size of the elementary blocks in a half empirical way and he found that they contain in the case of rocksalt and in

many other cases about 10,000 atoms each. As Smekals considerations enable us to understand a great number of facts it has to be concluded that the formation of cracks and blocks cannot be of a purely accidental nature. Otherwise, the surface cracks should occur in all kinds of different sizes on different samples. But then, it is impossible to understand why the technical breaking strength is a relatively well-defined quantity, as the different samples of a crystal would break on application of widely varied specific stresses. It is possible, indeed, to justify the above views on mosaic crystals on a more fundamental basis.

(*c*) *On the Theory of Mosaic Crystals.*—In a paper already mentioned, the author showed that the maximum lateral contraction γ on extenson is 5.4% for rocksalt. Calculations of the same kind have recently been published by Lennard-Jones[8] who also found that for the alkalihalides γ is 6% approximately. This means that considering the ions of one lattice plane only, they will try to arrange themselves in a lattice characterized by spacings which are 6% smaller than the spacing in the solid crystal. This same tendency to contract is also exhibited by the surface planes, although in a lesser degree.

Now the equilibrium configuration of the crystal is one of minimum energy.‡ But this configuration according to the above is characterized by a lattice spacing which is constant in the interior of the crystal and decreases toward the surface. Now it is easily seen that the surface cannot contract as a whole, but it will do so in patches of a definite average size between which cracks will be left open. The linear extension L of such a patch corresponds roughly to: $L = 100R/\gamma$. This is approximately 100 Å for rocksalt. A much larger extension is excluded because of the fact that otherwise ions of a certain sign in the top layer would come to lie above ions of the same sign in the lower less contracted layers. This then would tend again to increase the energy. Now let $\epsilon.S$ be the decrease in energy corresponding to the contraction of a patch of surface S. Notice, also, that the largest cracks will be those which are formed adiabatically. Then the new surface S' (normal to the old) which can be formed at the expense of the energy gained by the contraction of S will be $S' = S.\epsilon/\sigma$. Now ϵ can easily be calculated from the theory of the heteropolar crystals. For NaCl the value 220 ergs/cm.^{2} is obtained. Although this value is undoubtedly somewhat too large when applied to the surface of a crystal, it is nevertheless evident that S' is approximately equal to S. It should be stated also that not the entire surfaces of the crack will consume an energy σ erg/cm.^{2} for its formation, as at the point P_0 (see figure) the surface energy evidently must become zero. Assuming then, for instance, an average value $\sigma/2$ for the surface energy per cm.^{2} along P_1P_0 we have according to the above this approximate relation for the depth of the crack $P_1P_0 = 2\ L/4 \sim 50$ Å. The surface of a crystal

will then exhibit an appearance as approximately represented in figure 1. The dimensions given are those which we would have to expect for the largest cracks.

One further conclusion which can be drawn from the numerical relations given above is this: The crystal will not only crack on the surface, but also exhibit a great tendency for block formation all through its interior when not controlled properly during its growth. This follows from the fact that the energy gained from the contraction of a surface is of the same magnitude as the surface energy. It should be possible at least partially to avoid the formation of a mosaic structure in the crystal by growing it under very well-controlled conditions. But it is then to be expected from the theory that such crystals will be very unstable against mechanical and thermal disturbances. There are a number of facts known which seem to justify the above conclusions. A very instructive experiment is this. Certain organic crystals grown in the saturated solution are stable as long as they are entirely covered by the liquid. They break off immediately, however,

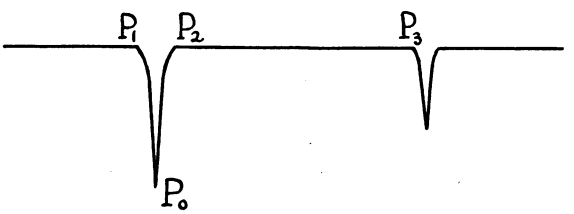

FIGURE 1

$P_1P_2 \sim 8Å$ $P_2P_3 \sim 100Å$ $P_0P_1 \sim 50Å$.

as soon as the surface becomes dry. The fact that very thin glass and quartz fibers show a high strength just after formation, followed by a gradual decrease, might be interpreted in the same way. It is probable, also, that the instability of the properties known as cold hardening falls into this category.

It can now be understood that the technical breaking strength will be a well-defined quantity. It will be determined by the size and shape of the largest cracks, which in turn may be obtained in principle by the above considerations. To account for the ratio of the technical to the ideal strength will be the aim of a more rigorous treatment of the problem involved.

It is also comprehensible now why an apparently trivial conditioning of the surface like wetting rocksalt with water produces the enormous strengthening mentioned before. We know from the interionic theory of strong electrolytes, that the ions in the saturated solution will influence the ions in the solid surface in nearly the same way as the ions arranged in lattice planes below the surface. The minimum of the free energy

will be obtained with an almost smooth surface. The crystal, therefore, is much strengthened as far as rupture is concerned. It should be said, however, that the application of great stresses will produce slipping of the different blocks in the inner parts of the crystal. This process leads to the cold hardening, a phenomenon for which a proper theory is not yet given.

As to the number of particles constituting one of the elementary blocks it follows from the dimensions given in figure 1 that this number is approximately 10,000. This is exactly the number which Smekal has deduced in a more phenomenological way.

(*d*) *Generalization of the Theory.*—In the case of heteropolar crystals a rigorous mathematical treatment of the block formation seems possible. We have no quantitative knowledge, however, about the forces of cohesion in homopolar crystals. A qualitative generalization of the considerations given is nevertheless possible.

The formation of cracks and blocks in crystals must be a very general phenomenon as it is essentially related to the existence of a lateral contraction on extension. These qualitative statements can be made on the size of the elementary cracks and blocks:

(1) The surface of the elementary blocks will increase with increasing lattice constant. This is due to the fact that a relative shift of half a lattice constant (or eventually another simple fraction of R) represents a configuration of a relative maximum of the potential energy.

(2) The surface of the blocks will decrease with an increasing tendency to a lateral contraction of the lattice plane forming this surface. An empirical estimate of this tendency can be obtained by studying the geometrical and energetic aspects of the lateral contraction of the crystal on extension.

(3) The depth of the largest cracks will essentially be determined by the ratio of the energy of contraction ϵ to the surface of energy σ.

(*e*) *Additional Remarks.*—In general the cracks will be distributed irregularly over the surface of a crystal. It might be expected, however, that a surface grown under properly controlled conditions would show some regularity in the distribution of the blocks. This then suggests the possibility of using such a surface as a grating for soft x-rays, the grating constant being for rocksalt approximately 100 Å. In certain cases like Bi we should expect blocks of considerable size, so that interference fringes might eventually be obtained with visible light.

A very nice proof of the existence of cracks in single crystals of Bi was given by Kapitza.[9] He showed that on application of external pressure, the cracks could be closed so that the electric resistance was diminished correspondingly.

Some very interesting conclusions are also suggested in regard to the

chemical imperfections of crystals. Suppose that we have two kinds of atoms which do not form a mixed crystal. If a crystal which is built up by atoms of the first type actually contains atoms of the other kind it is evident that these atoms must be absorbed along the cracks. This fact combined with our considerations provides a satisfactory explanation for the following very interesting phenomenon. It is known that the amount of absorbed gas in a metal varies in this way with the temperature. The amount of absorbed gas increases when the temperature is raised. At the melting point a sudden jump occurs inasmuch as the melt absorbs much more gas than the solid. Sometimes the absorption curve shows a minimum considerably below the melting point. From our theory it follows that there are two effects which have to be taken into account. Firstly, the amount of gas ρ absorbed per unit surface will decrease when the temperature is raised. But the total surface S available for absorption on the other hand will increase with T. In section d_3, it was shown that $S \propto \epsilon/\sigma$. Now, ϵ will depend very little on temperature, as it is essentially related to the lateral contraction. The surface tension σ, on the other hand, decreases with increasing T so that S increases with T. The total amount of absorbed gas $S.\rho$ varies with T precisely as required by the experiments. To get the number of atoms n per elementary block just below the melting point, we propose this approximate estimate. In the melt, the absorbed gas atom can be associated with any one of the N metal atoms present. The surface S_m available for the absorption, therefore, is: $S_m = 4\pi r^2 . N$, where r is of the order of the diameter of an atom. The total surface S of the elementary blocks in the solid just below the melting point is of the order $S = 6N/n \left(\frac{4\pi}{3} nr^3\right)^{2/3}$. The ratio of the amount of absorbed gas in the solid (G) and in the melt (G_m) is:

$$G_m/G = S_m/S = \frac{1}{2}\left(\frac{4\pi}{3} n\right)^{1/3} \sim 0.8n^{1/3}.$$

For the absorption of oxygen in silver (10) it is $G_m/G \sim 20$. Therefore, $n \sim 15{,}000$, which is of the same order of magnitude as the value required by the theory. This satisfactory agreement supports the statement made in the beginning, that the chemical impurities in crystals are very essentially related to the mechanical imperfections of the crystal structure.

I am indebted to Dr. A. Goetz of this laboratory for having called my attention to many experimental facts related to the problem under discussion.

* NaCl in the molten state has at 800°C. a surface tension $\sigma \sim 100$ erg/cm^2.

† See, however, the objections raised by Polanyi in *Naturwissenschaften*, **1928**, p. 1043.

‡ Actually the free energy has to be a minimum. It is easy to show, however, that the difference between the energy and the free energy is negligible in this case.

[1] Polanyi, M., *Zeits. Phys.*, **7**, 323, 1921.

[2] See for instance, Born, M., *Encyklopaedie Math. Wissenschaften*, V_3, Heft. 4.

[3] Zwicky, F., *Physik. Zeits.*, **24**, 131, 1923.

[4] Joffe, A., Kirpitschewa, M. W., and Lewistzky, M. A., *Zeits. Physik*, **22**, 286, 1924. Muller, H., *Physik. Zeits.*, **25**, 223, 1924. Ewald, W., and M. Polanyi, *Zeits. Physik*, **28**, 29, 1924.

[5] Griffith, A. A., *Proc. Int. Congr. Appl. Mechanics*, Delft, **1924**, 55.

[6] Smekal, A., *Zeits. techn. Physik*, **7**, 535, 1926; **8**, 561, 1927, and several other papers.

[7] See for instance, the article of P. P. Ewald in *Handbuch Physik*, **24**, 280 (Ed. J. Springer, Berlin).

[8] Lennard-Jones, J. E., and B. M. Dent, *Proc. Roy. Soc.*, **121**, 247, 1928. In this paper the authors also remark that the lateral contraction might cause cracking of the surface of crystals.

[9] Kapitza, P., *Proc. Roy. Soc.*, **119**, 358, 1928.

[10] Steacie, E. W. R., and F. M. G. Johnson, *Proc. Roy. Soc.*, **113**, 542, 1926.

THE MECHANISM OF SPARK DISCHARGE

BY LEONARD J. NEUMAN

PHYSICAL LABORATORY, UNIVERSITY OF CALIFORNIA

Communicated February 11, 1929

In attempting to account for the ionization required for the initiation of a self-sustained electrical discharge, J. S. Townsend[1] developed a theory of the electric spark. While the cumulative ionization of the gas at high fields by electrons constitutes part of the mechanism of the spark, Townsend has shown that for a self-sustained discharge it is essential that electrons be liberated in the neighborhood of the cathode. From his investigations on the ionization current between parallel plates produced by high electrical fields Townsend concluded that for sufficiently high values (X/p), (X = electric field strength, p = gas pressure) the positive ions could ionize the gas molecules by impact. As a result of these researches he developed his well-known equation for spark discharges. At that time experiment seemed to indicate that the sparking potential was a function of the gas and the electrical field strength and was practically independent of the electrode material, consequently Townsend's equation was quite generally accepted. Later Townsend[1] extended his theory to include ionization by positive ions at the surface of the cathode, an effect that could conceivably take place at low pressure when the positive ions had little chance to strike gas molecules near the cathode. In 1922 Holst and Oosterhuis[2] found that the sparking potential in neon (p of order of a few mm.) varied in the ratio of 1–3 when the cathode material was changed from carbon to rubidium or caesium. Assuming a uniform